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Thermodynamic properties of liquid AlMg alloys

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Abstract : A statistical thermodynamic theory in conjunction with the complex formation model, has been used to investigate the thermodynamic properties of liquid AlMg alloys. Thermodynamic properties such as free energy of mixing, heat of mixing and entropy of mixing have been reproduced by our expressions. Concentration-concentration fluctuations at the long-wavelength ($S_{cc}(0)$) limit have been obtained to investigate the stability and structural information about liquid AlMg alloys. The study of chemical short range order parameter (α_1) has been carried out to quantify the degree of order. The study reveals that liquid AlMg alloy is a weak interacting system. It is to mention that various factors such as size difference and electronegativity difference are too small to account for the asymmetric behaviour in this system. The observed asymmetry suggests that Al_3Mg_2 complexes are formed in the liquid AlMg alloy.

Keywords : Liquid AlMg alloys, thermodynamic properties, concentration fluctuations, chemical short range order, electronegativity.

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1. Introduction

Aluminium alloys are of technological [1] and industrial [2] importance. Al-based materials have received significant research interest with the aim to develop a new family of high-strength materials [3]. High strength aluminium alloys consist of at least five (Li, Ca, Cu, Mg, Si) significant alloying elements. There is a great interest in Al-rich alloys especially due to improved mechanical properties of nano structural materials [4]. Kawakami [5] and Batalin *et al* [6] have measured the integral enthalpy of mixing in the liquid phase of AlMg calorimetrically. These measurements deviate markedly from each other for concentrations higher than $C_{Mg} = 0.4$. These values have been derived [7,8] from partial quantities using the Gibbs Duhem relation considering the integral excess entropy. Moreover, different investigators [9,10] have used different lattice stabilities and as such, its extension to ternary and higher order aluminium alloy system becomes difficult. There is a large scatter in experimental values reported for liquid AlMg alloy. However, these deviations are a result of the experimental error. Of the previous evaluation reported in the literature, the evaluation by Saunders [9] for liquid AlMg alloy was the most extensive and satisfactory.

Asymmetry in various properties of mixing of AlMg molten alloys, though free energy of mixing G_M is not very large ($G_M^{XS} = -0.15$ KJ/mol) is noticed around equiatomic composition. The anomalous behaviour of mixing properties of liquid AlMg alloys may not be attributed to the low size factor (Ω_{Mg}/Ω_{Al}, Ω is the volume) 1.34. The electronegativity (EN = 1-exp (–0.25 d^2), d is the difference in the EN values of the elements) values of 0.023 for Al-Mg yield a weaker ionic character in comparison with 0.51 for well-known ionic system CsAu [11]. The linear decrease in the melting temperature of the alloy and flattened minimum in the intermediate region as observed in the phase diagram [1,7,12–16] suggest that the intermetallic compound Al_3Mg_2 exists in the solid phase. Results from different authors [1,7,12–16] are in good agreement within the experimental error. The formation of compounds in solid phase led many theoreticians [17–21] to believe that chemical complexes, pseudomolecules and privileged group of atoms might exist in molten state. Various theoretical models [22–25]

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based on the above assumption, are being used to investigate alloying behaviour of such type of binary molten alloys.

Asymmetry in the free energy of mixing G_M and the heat of formation H_M are responsible for promoting complex formation in the liquid alloys, but these properties need not necessarily imply complex formation [21]. Hence, the concentration fluctuations in the long wavelength limit $S_{cc}(0)$ are one of the most powerful microscopic functions for understanding the nature of interatomic interactions. Chemical short-range order parameter, α_1 is evaluated to quantify the degree of order.

In this study, a statistical thermodynamic model based on complex formation (μ Al + ν Mg $\Leftrightarrow$ $Al_\mu Mg_\nu$, $\mu = 3$, $\nu = 2$) has been used to calculate the interdependence of various thermodynamic properties, such as the free energy of mixing, the heat of mixing, the entropy of mixing, concentration fluctuations at long wavelength limit, the chemical short range order parameter of liquid AlMg alloys. This concept has been used successfully to explain the mixing properties [21,25–27] of a variety of binary liquid alloys.

2. Formalism

2.1. *Properties of mixing :*

The grand partition function of an alloy consisting of N_1 number of A atoms and N_2 number of B atoms may be expressed in terms of the configurationally energy,

$$\Xi = \Sigma(q_1(T))^{N_1}(q_2(T))^{N_2} \exp\{(\mu_1 N_1 + \mu_2 N_2 + E)/K_B T\} \quad (1)$$

where $q_i(T)$ and μ_i are the atomic partition functions and the chemical potential of the i-th ($i = 1, 2$) species, respectively. K_B and T refer, respectively, to the Boltzmann's constant and the absolute temperature. Eq. (1) can be solved [28] in the framework of the quasi-lattice theory to obtain various expressions for the thermodynamic and microscopic functions. After performing some algebra [29], we may obtain the free energy of mixing as

$$G_M = G_M^{XS} + RT \Sigma C_i \ln C_i, \quad (2)$$

$$G_M^{XS} = C_1 C_2 W + \phi_{12} W_{12} + \phi_{11} W_{11} + \phi_{22} W_{22}, \quad (3)$$

$$\phi_{12} = C_1 \mu^{-1} C_2 \nu^{-1}(2 - C_1 \mu^{-1} C_2 \nu^{-1}),$$

$$\phi_{11} = C_1 \mu^{-2} C_2 \nu (2 - C_1 \mu^{-2} C_2 \nu), \quad \mu \geq 2,$$

$$\phi_{22} = C_1 \mu C_2 \nu^{-2}(2 - C_1 \mu C_2 \nu^{-2}), \quad \nu \geq 2, \quad (4)$$

where W is the ordering energy and W_{12}, W_{11}, W_{22} are the interaction energies. C_1 and C_2 are the concentrations of the first and second species of the alloy. ϕ_{ij} is probability of finding the i–j bond as a part of the complex. For $\mu = 3$ and $\nu = 2$,

$$\phi_{12} = 13C_1/420 + 2C_1^3/3 - 3C_1^4/2 + 3C_1^5/5 + 2C_1^6/3 - 5C_1^7/7 + C_1^8/4,$$

$$\phi_{11} = -53C_1/840 + 2C_1^3 - 5C_1^4/4 + 6C_1^5/5 - C_1^6 + 4C_1^7/7 - C_1^8/8,$$

$$\phi_{22} = 23C_1/280 - C_1^4/2 + 2C_1^5/5 + C_1^7/7 - C_1^8/8. \quad (5)$$

The heat of formation H_M can be obtained from eq. (2) and the relation

$$H_M^{XS} = G_M^{XS} - T(\partial G_M^{XS}/\partial T)_{P,C,N}, \quad (6)$$

Eqs. (2) and (6) yield

$$H_M^{XS} = C_1 C_2 (W - T(\partial W/\partial T)) + \sum_{i,j}^{1,2} \phi_{ij} (W_{ij} - T(\partial W_{ij}/\partial T)) \quad (7)$$

The entropy of mixing S_M is given by

$$S_M = (H_M - G_M)/T. \quad (8)$$

2.2. *Concentration fluctuations in the long wavelength limit, shortrange order parameter and the activity coefficient :*

Concentration fluctuations in the long wavelength limit $S_{CC}(0)$ have been widely used [21,30,31] to understand the alloying behaviour of liquid binary alloys. $S_{CC}(0)$ is related to G_M as

$$S_{CC}(0) = RT (\partial^2 G_M/\partial C_1^2)^{-1}_{T,P,N}. \quad (9)$$

Using eq. (2) the value of $S_{CC}(0)$ for $\mu = 3$ and $\nu = 2$ is given by

$$S_{CC}(0) = C_1 C_2 \{1 + C_1 C_2 (RT)^{-1}[-2W + 2C_1(2 - 9C_1 + 6C_1^2 + 10C_1^3 - 15C_1^4 + 7C_1^5)W_{12} + C_1(4 - 15C_1 + 24C_1^2 - 30C_1^3 + 24C_1^4 - 7C_1^5) W_{11} + C_1^2(-6 + 8C_1 + 6C_1^3 - 7C_1^4)W_{22}]\}^{-1}. \quad (10)$$

The Warren-Cowley [32,33] short-range order parameter (α_1) is evaluated to quantify the degree of order and it is computed theoretically [21,22,31] as

$$\alpha_1 = (S - 1)/(S(Z - 1) + 1), \quad (11)$$

$$S = S_{CC}(0)/S_{CC}id(0), \quad (12)$$

$$S_{CC}id(0) = C_1 C_2. \quad (13)$$

Here, Z is the coordination number, which is taken as 10 for our purposes.

The activity coefficients are given by

$$\ln \gamma_i = (K_B T)^{-1}[G_M + (1 - C_i)(\partial G_M/\partial C_i)]. \quad (14)$$

Eq. (2) gives the values of activity coefficients for $\mu = 3$ and $\nu = 2$ as

$$\ln \gamma_1 = (1/K_BT)\,[W(1 - C_1)^2 + W_{12}(13/420 + 2C_1^2 - 22C_1^3/3 + 15C_1^4/2 + 8C_1^5/5 - 25C_1^6/3 + 44C_1^7/7) + W_{11}(-53/840 + 2C_1^2 - 19C_1^3/3 + 39C_1^4/4 - 54C_1^5/5 + 9C_1^6 + 31C_1^7/7 + 7C_1^8/8) + W_{22}(23/280 - 2C_1^3 + 7C_1^4/2 - 8C_1^5/5 + C_1^6 - 13C_1^7/7 + 7C_1^8/8)]. \quad (15)$$

$$\ln \gamma_2 = (1/K_BT)\,[C_1^2 W + W_{12}(-4/3 + 9C_1/2 - 12C_1^2/5 - 10C_1^3/3 + 30C_1^4/7 - 7C_1^5/4)\,C_1^3 + W_{11}(-4/3 + 15C_1/4 - 24C_1^2/5 + 5C_1^3 - 24C_1^4/7 + 9C_1^5/8)C_1^3 + W_{22}(3/2 - 8C_1/5 - 6C_1^3/7 + 7C_1^4/8)\,C_1^4]. \quad (16)$$

2.3. Viscosity :

Various expressions [34–36] are available in the literature for the calculation of viscosity (η) of binary liquid alloys. The expression given by Kucharsky [35] has been used here to investigate the viscosity of liquid Al-Mg alloys.

$$\eta = C_1V_1/V(v_1/v)^2\,\gamma_1^p\eta_1 + C_2V_2/V(v_2/v)^2\gamma_2^p\eta_2, \quad (17)$$

$$= C_1V_1^{1/3} + C_2V_2^{4/3}/V_1, \quad (18)$$

$$v_2 = C_2V_2^{1/3} + C_1V_1^{4/3}/V_2, \quad (19)$$

$$v = C_1V_1^{1/3} + C_2V_2^{1/3}. \quad (20)$$

V_i (i = 1, 2) and γ_i are, respectively, the partial molar volumes and the activity coefficients of the constituent species of the liquid binary alloys. η_1 and η_2 are the viscosities of the pure component, V is the volume of the alloy and p is a fitted parameter.

3. Results and discussion

3.1. Properties of mixing :

It is clear from Section 1 that the likely complex to be formed in liquid AlMg alloys is Al_3Mg_2. G_M of AlMg ($G_M/RT < -3.0$) system is low which indicates the weaker tendency of complex formation. This means that the value of W should be smaller. The values of W and W_{ij} were adjusted through computer simulations to get the concentration dependence of G_M through eq. (2). The energy parameters for liquid AlMg alloys at T = 1073 are found to be

$$W/RT = -0.76,\ W_{12}/RT = -1.88,\ W_{11}/RT = -0.24,$$

$$W_{22}/RT = -0.18.$$

The computed values of G_M *versus* concentration are shown for AlMg liquid alloy in the lower part of Figure 1 together with the experimental observations [7]. Figure 1 shows that the values of G_M are negative through the whole concentration range and the evaluated values are in agreement with the experimental values.

The heat of mixing and entropy of mixing of AlMg

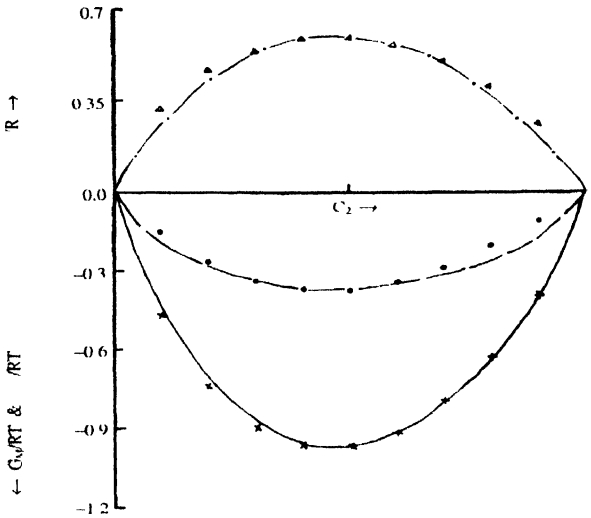

Figure 1. Upper part S_M/R — Theoretical, Δ Expt. [7]; Lower part G_M/RT – Theoretical, X Expt. [7], H_M/RT – – Theoretical, · Expt. [7].

liquid alloy have been computed to see the variation of energy parameters with temperature. It can be observed that the concentration-dependence of H_M can be explained if we consider the temperature dependence of the energy parameters for AlMg liquid alloys. These are given as

$$\partial W/\partial T = -2.6R,\ \partial W_{12}/\partial T = -0.4R,\ \partial W_{11}/\partial T = 0.24R,$$

$$\partial W_{22}/\partial T = 3.4R.$$

The evaluated values of H_M [eq. (7)] and S_M [eq. (8)] are plotted as a function of concentration in the lower and upper part, respectively, of Figure 1 alongwith the experimental values [7]. Like experiment, H_M is negative throughout the whole concentration range. There is a reasonable agreement between theory and experiment. The evaluated values of S_M are positive at all concentrations like the experimental values. The positives values of S_M throughout the whole concentration range show the existence of atomic order in liquid AlMg alloys.

3.2. Concentration fluctuations in the long wavelength limit, shortrange order parameter and activity coefficient :

The values of $S_{CC}(0)$ and α_1 have been computed *via* eq. (10) and (11) respectively and are shown in Figure 2. The experimental values of $S_{CC}(0)$ are obtained from measured activity data [7]. From $S_{CC}(0) < S_{CC}id(0)$, the existence of chemical ordering leading to complex formation is expected. $\alpha_1 < 0$ corresponds to unlike atoms pairing as nearest neighbour. Figure shows that Al-Mg alloy is more ordered towards Al-rich end. The activity coefficients calculated

through eq. (14) are tabulated in Table 1 along with experimental values [7]. The values are in fair agreement.

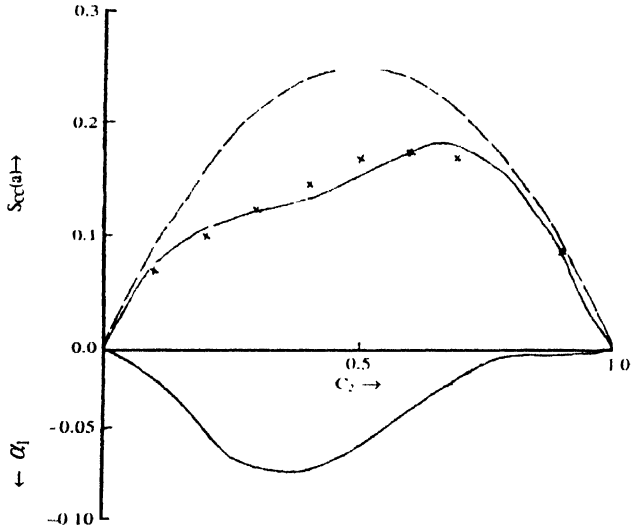

Figure 2. Upper part $S_{cc}(0)$ —Theoretical, X Expt. From activity data [7], – – ideal; Lower part α_1.

Table 1. Activity coefficients of Al (γ_1) and Mg (γ_2) in AlMg liquid alloys at 1073 K.

C_2	γ_1		γ_2	
	Present	Expt. [7]	Present	Expt. [7]
0.1	0.994	0.971	0.236	0.301
0.2	0.952	0.900	0.380	0.464
0.3	0.870	0.817	0.548	0.623
0.4	0.769	0.732	0.714	0.763
0.5	0.675	0.658	0.847	0.871
0.6	0.602	0.599	0.933	0.942
0.7	0.557	0.555	0.974	0.982
0.8	0.534	0.530	0.988	0.987
0.9	0.514	0.522	0.995	1.000

3.3. Viscosity :

The linear volume ($C_1V_1 + C_2V_2$) of the alloy based on the density data of Smithell's Metals Reference Book [37] has been considered here to calculate the viscosity of liquid Al-Mg alloy. The viscosity of the component elements of the alloy have also been taken from the same book [37]. The computed values are shown in Figure 3. Different values of p have been used for the calculation of η to see the effect of the fitted parameter. It is to mention that the complex forming liquid alloys show maxima [36,38] in those composition ranges where intermetallic compounds are formed. The maxima in the viscosity is found with $p = -0.8$

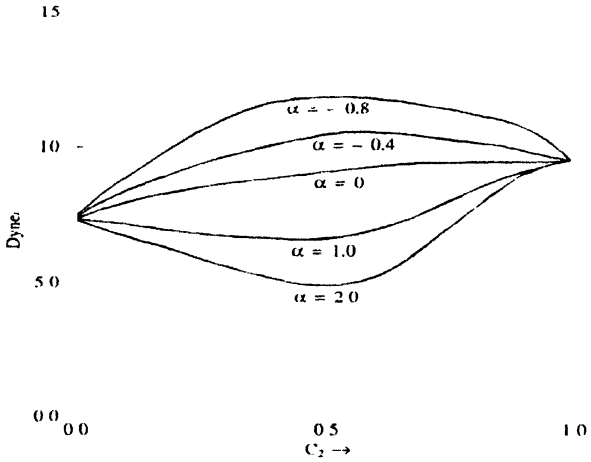

Figure 3. Viscosity of liquid AlMg alloy at 1073 K.

around the same composition where $S_{cc}(0)$ is minimum. With increasing negative values of p, the maximum shifts towards Mg-rich end and the minimum shifts towards Al-rich end with the increasing positive values of p. The theoretical values have not been compared with the experimental values as they are not available to the best of our knowledge.

4. Conclusion

The concentration-dependence mixing properties of AlMg liquid alloys have been explained successfully with the assumption of Al_3Mg_2 complexes in the melt. The same energy parameters have been used for the evaluation of mixing properties, $S_{cc}(0)$ and α_1. The asymmetry in all the cases was found around the same composition range. The low value of the free energy of mixing indicates that Al-Mg system is a weak interacting system. The same energy parameters have been used to calculate the bulk properties and viscosity. The properties suggest the compound formation in Al-Mg liquid alloys.

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